Preparation and characterization of ester-derived $BaFe_{12}O_{19}$ powder

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Ultrafine $BaFe_{12}O_{19}$ powder with crystallite sizes less than 200 nm was prepared via a citric acid precursor method. Citric acid was added into an aqueous solution, containing nitrates of Ba^{2+} and Fe^{3+} in a stoichiometric ratio to form barium ferrite, to chelate metallic ions in the solution. The pH of aqueous solutions was adjusted with NH_4OH. After ethylene glycol was added into the solution and the system temperature was raised, esterification and dehydratation led to the formation of solid ester precursor. The distribution and contents of metallic ions in the ester are affected by the [citric acid]/[metallic ions] molar ratio used and the pH of starting solutions. When the ester-precursor obtained at pH = 9 with [citric acid]/[metallic ions] = 1.5 was used, crystalline $BaFe_{12}O_{19}$ appeared at temperatures as low as 923 K, and pure barium ferrite was obtained at 1073 K. According to the experimental results obtained, the reaction mechanism involved in the pyrolysis of esters is proposed and discussed.

I. INTRODUCTION

Hexagonal barium ferrite ($BaFe_{12}O_{19}$) is well established as a high-performance permanent magnetic material,[1] due to its fairly large magnetocrystalline anisotropy, high Curie temperature, and relatively large magnetization, as well as excellent chemical stability and corrosion resistivity. In recent years, barium ferrite has been extensively studied for advanced recording applications, such as disk drivers and video recorders.[2,3]

The characteristics of $BaFe_{12}O_{19}$ particles are very important for manufacturing permanent ceramic magnets because of their influence on the microstructure of final products. The conventional solid-state method for preparing $BaFe_{12}O_{19}$ is to fire an appropriate mixture of α-Fe_2O_3 and $BaCO_3$ at very high temperatures (1423 to 1523 K). The resulting powder is then ground to reduce its particle size.[4] Although high-temperature firing assures the formation of the required ferrite phase, larger particles (>1 μm) are often obtained in this firing process. It has been shown that the theoretical intrinsic coercivities of ferrites can be approached only when the particle sizes are below 1 μm.[5] On the other hand, grinding may introduce impurities into the powder and cause strains in the crystal lattices, which all have unfavorable effects on the magnetic properties. Several unconventional techniques, such as the coprecipitation method,[6–8] the glass crystallization method,[9–11] the hydrothermal technique,[12] and the precursor method,[13,14] have been used or are under development for preparing ultrafine barium ferrite particles. The most important feature of these methods is the use of liquid media to intimately mix the required metallic constituents on an ionic level. Mixing the required metallic ions homogeneously on the atomic scale can form the required oxide phase(s) at relatively low temperatures, resulting in small particles.

Jacobao *et al.*[6] and Ross[8] used the coprecipitation method to prepare barium ferrite and showed that by heating the coprecipitates at relatively low temperatures ($\leqslant$1073 K), submicron $BaFe_{12}O_{19}$ particles can be obtained. Kubo *et al.*[11] prepared $BaFe_{12}O_{19}$ using a glass crystallization method. The particles obtained were less than 0.1 μm and were single domain hexagonal thin platelets with easy magnetization axis normal to their plane. Shirk *et al.*[9] also showed that the glass crystallization method could allow barium ferrite to uniformly nucleate and crystallize in a homogeneous matrix at elevated temperatures, resulting in ultrafine particles with sharp particle size distribution and the corresponding crystals well separated from each other. On the other hand, Barb[12] obtained barium ferrite in hydrothermal conditions from a water suspension of α–FeOOH and $Ba(OH)_2 \cdot 8H_2O$ at a temperature of about 588 K.

The citric acid precursor method originated from the Pechini method. Pechini developed this method in 1967 and applied for patent in the United States (Patent No. 3 330 697). In the precursor method, the metallic salts are dissolved in water to have the required metallic ions mix well. The metallic ions are then chelated by a poly-acid

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(e.g., critic acid), and esterification of chelated cations is carried out by adding poly-alcohol (e.g., ethylene glycol) at appropriate temperatures. After dehydration, a solid ester precursor with well-mixed metallic ions can be obtained. The solid precursor is subjected to proper heat treatment to form the final ceramic particles. Lucchini et al.[15] showed that using pectic acid to chelate barium and iron ions in an aqueous solution of nitrates and heating in air at 973 K can produce crystalline barium ferrite with particle sizes less than 1 μm in diameter. In the present study, citric acid was adopted as the chelating agent for metallic ions, and after esterification and pyrolysis, submicron barium ferrite powder was produced and characterized.

II. EXPERIMENTAL PROCEDURE

The following chemicals were used in our experiments: iron nitrate nonahydrate (99% purity, ACROS, Belgium), barium nitrate (99% purity, SHOWA, Japan), anhydrous citric acid (99% purity, SHOWA, Japan), ethylene glycol (99.97% purity, TEDIA, Fairfield, OH) and ammonium hydroxide (29.5% NH_3, TEDIA, Fairfield, OH). $Ba(NO_3)_2$ and $Fe(NO_3)_3 \cdot 9H_2O$, in a stoichiometric ratio to form $BaFe_{12}O_{19}$, were dissolved in de-ionized water to form the required aqueous solution of 0.04 M. To chelate Ba^{2+} and Fe^{3+} in the solution, citric acid was added into the prepared aqueous solution. The pH of solutions was adjusted with NH_4OH and varied from approximately 1 to 9. Esterification of the solution was carried out by introducing ethylene glycol into the solution and raising the solution temperature to 353 K. The amount of ethylene glycol added was 1.5 times of the number of moles of citric acid in the solution. Esterification in the solution was likely through polycondensation mechanisms since citric acid (with three carboxylic groups) and ethylene glycol (with two hydroxyl groups) are polyfunctional acid and alcohol, respectively. Esterification and solvent evaporation at 353 K resulted in a highly viscous liquid. The viscous liquid was then dried at 393 K in an oven. It is to be noted that the volume of the specimen obtained with the addition of NH_4OH in the starting solution was dilated during drying. After drying, the porous solid ester precursors were obtained.

The solid ester precursors were pyrolyzed at 623 K, followed by different heat treatment temperatures (i.e., 923, 973, 1073, and 1173 K). The heated specimens were then characterized by x-ray diffraction (XRD; M03X-HF, Mac Science, Japan), scanning electron microscopy (SEM; S-800, Hitachi, Japan), transmission electron microscopy (TEM; H-700, Hitachi, Japan), thermogravimetric analysis (TGA; Ger-TGA 2950, Netzsch, Germany), and differential scanning calorimetry (DSC; HT-DSC 404, Netzsch, Germany). Effects of pH and [citric acid]/[metallic ions] molar ratio of the starting solution, as well as heating temperatures, on the characteristics of resultant particles were studied.

III. RESULTS AND DISCUSSION

Figure 1 gives XRD patterns of the particles obtained at 1073 K with four different pH values of the starting solution. For these specimens, molar ratios of citric acid to metallic ions in starting solutions were fixed at 1.5. At pH = ~1 (i.e., no NH_4OH was added to the starting solution.), the particles were composed of α-Fe_2O_3, $BaFe_{12}O_{19}$, and BaO. At pH = 7 and 9, pure $BaFe_{12}O_{19}$ particles were obtained. Raising the pH of starting solutions by adding NH_4OH not only increased the amount of $BaFe_{12}O_{19}$ in particles but also increased the crystallinity of barium ferrites. The degree of chelation of metallic ions, by carboxylic groups ($COOH^-$), in the starting solution is responsible for the uniformity of metallic constituents in the ester precursor after esterification. At higher pH conditions, more citric acid is ionized, more carboxylic groups can be available to chelate the metallic

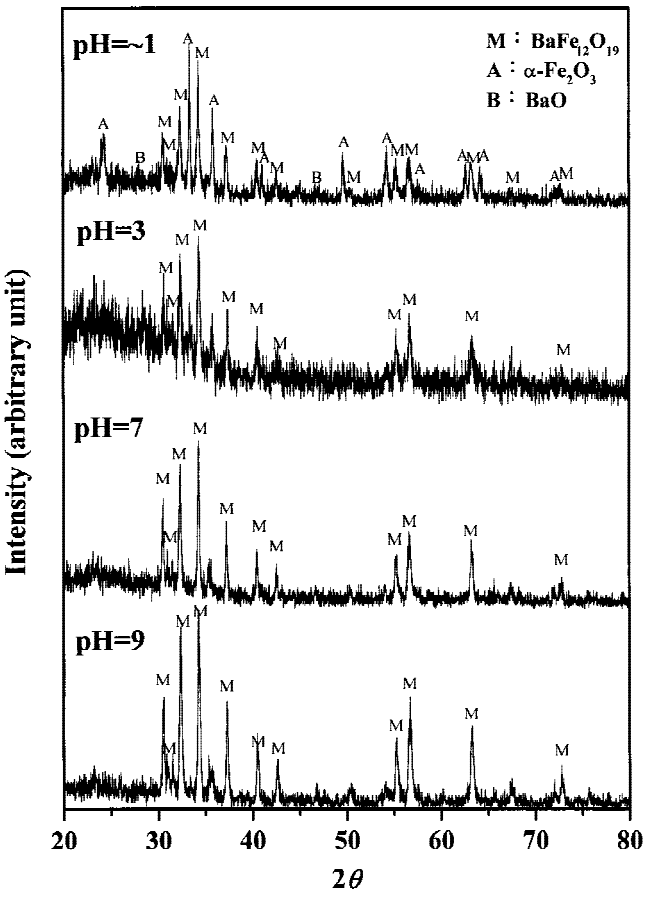

FIG. 1. XRD patterns for the specimens ([citric acid]/[metallic ions] = 1.5) obtained at 1073 K, with four different pH values of the starting solution.

ions in the solution, and higher uniformity of metallic elements in the ester can be attained. Figure 2 shows TEM photomicrographs of the specimens discussed in Fig. 1. At pH = 7 and 9, hexagonal platelike barium ferrite crystallites with sizes less than 200 nm were obtained. It is also apparent that the sizes of $BaFe_{12}O_{19}$ crystallites increased with pH. SEM analysis indicated that the particles obtained were agglomerated, and the sizes of primary particles were much less than 500 nm.

To illustrate the importance of the [citric acid]/[metallic ions] molar ratio in the starting solution on the characteristics of derived particles, the molar ratio of citric acid to metallic ions in starting solutions was reduced to 0.5 and the experiment was repeated. Figure 3 shows XRD patterns of the specimens obtained after thermally treating at 1073 K for 3 h. Regardless of pH of the starting solution used, all particles were composed of α–Fe_2O_3, $BaFe_{12}O_{19}$, and BaO. At pH = ~1, 3, and 7, α–Fe_2O_3 was the major crystalline phase. The amount of crystalline $BaFe_{12}O_{19}$ increased with pH. The results indicated that at higher pH conditions $BaFe_{12}O_{19}$ is easier to form, which is due to a more complete chelation of the metallic ions in the solution. Although at pH = 9 barium ferrite became the major phase, α–Fe_2O_3 was still detected in this specimen. This result was ascribed to the deficiency of citric acid in the solution, so there were not enough carboxylic groups to chelate the required metallic ions.

The effects of the heating temperature for ester precursors on the derived particles are demonstrated in Fig. 4. The specimens were all prepared at pH = 9 with [citric acid]/[metallic ions] = 1.5 but subjected to different heating temperatures. At 623 K, small amounts of γ–Fe_2O_3, BaO, and $BaCO_3$ crystallites were detected. $BaFe_{12}O_{19}$ crystallites appeared at 923 K and became the major phase in particles after 973 K. At 923 K, γ–Fe_2O_3 allotropically transformed to α–Fe_2O_3. After 1073 K, only crystalline $BaFe_{12}O_{19}$ was detected. XRD analysis indicated that during heat treatment $BaCO_3$ was formed as an intermediate phase and disappeared at 1073 K or above, implying that $BaCO_3$ decomposed at temperatures around 1073 K. Although $BaFe_{12}O_{19}$ formed at 923 K, pure barium ferrite particles could not be obtained before the complete disappearance of $BaCO_3$.

To find out the exact thermal behavior of the prepared ester precursors, the specimen heated at 623 K was thermally analyzed by using DSC and TGA. Figure 5 gives

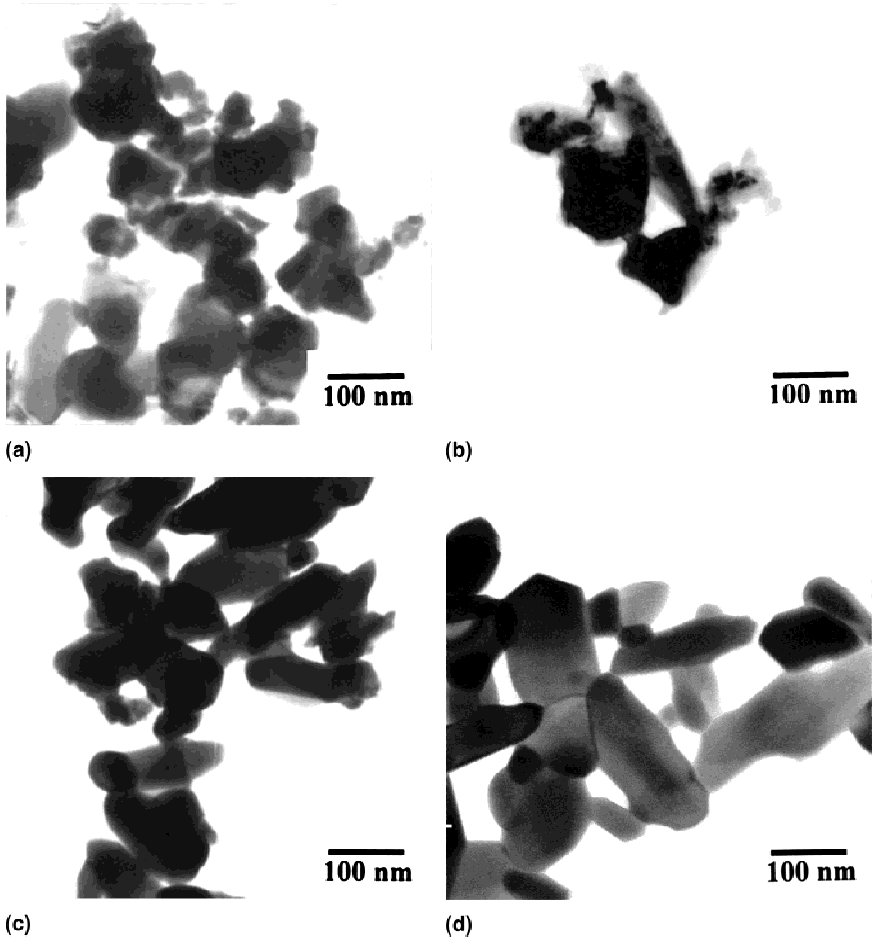

FIG. 2. TEM (×100 K) photomicrographs for the specimens ([citric acid]/[metallic ions] = 1.5) obtained after 1073 K, with the starting solution of (a) pH = ~1, (b) pH = 3, (c) pH = 7, and (d) pH = 9.

the corresponding thermal curves, with a heating rate of 10 °C/min and operating in stagnant air. Between 523 and 773 K, the sample experienced exothermic changes and the sample weight reduced about 11%. These exothermic changes were mainly due to the decomposition of esters. This indicates that heating the ester precursor at 773 K or above is necessary for complete decomposition of the esters prepared in this experimental condition. Depending on the interactions between metallic ions and carboxylic groups and the amounts of carboxylic groups and ethylene glycol available in the system, esters with different molecular weights and metal contents may be produced during esterification. Esters with different molecular weights and metal contents will give a wide temperature range for esters decomposition. Between 973 and 1073 K, slight weight loss was observed in the specimen. Comparison of the results obtained from the thermal analysis and XRD (Figs. 4 and 5) and reference to the results obtained by Moya *et al.*[16,17] suggest that the intermediate $BaCO_3$ phase reacted with α–Fe_2O_3 to form hexagonal ferrite or decomposed to BaO at 973–1073 K during heating.

According to the experimental results obtained in this study, it was postulated that after esterification and dehydration, the following reaction steps would occur in the obtained solid precursor during heating:

Step 1

$$(Fe^{3+}, Ba^{2+} - \text{esters}) \xrightarrow{\Delta} BaFe_{12}O_{19} + \text{gaseous products} \quad , \tag{1a}$$

$$(Fe^{3+} - \text{esters}) \xrightarrow{\Delta} \gamma - Fe_2O_3 + \text{gaseous products} \quad , \tag{1b}$$

$$(Ba^{2+} - \text{esters}) \xrightarrow{\Delta} BaCO_3 + BaO + \text{gaseous products} \quad , \tag{1c}$$

Step 2

$$6\gamma - Fe_2O_3 + BaO \xrightarrow{\Delta} BaFe_{12}O_{19} \quad , \tag{2a}$$

$$\gamma - Fe_2O_3 \xrightarrow{\Delta} \alpha - Fe_2O_3 \quad , \tag{2b}$$

$$BaCO_3 \xrightarrow{\Delta} BaO + CO_2 \quad , \tag{2c}$$

$$6\alpha - Fe_2O_3 + BaCO_3 \xrightarrow{\Delta} BaFe_{12}O_{19} + CO_2 \quad , \tag{2d}$$

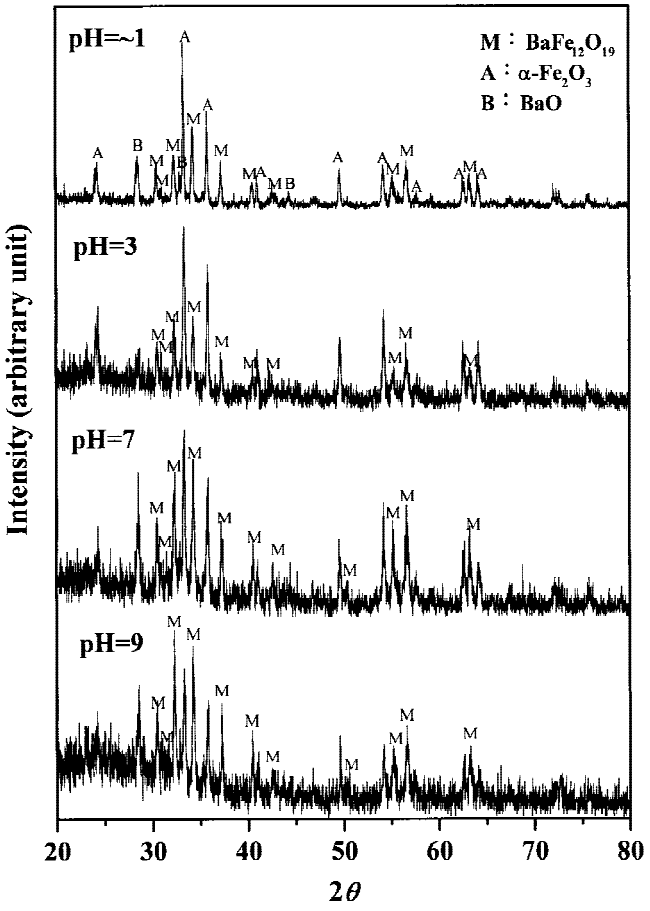

FIG. 3. XRD patterns for the specimens ([citric acid]/[metallic ions] = 0.5) obtained at 1073 K, with four different pH values of the starting solution.

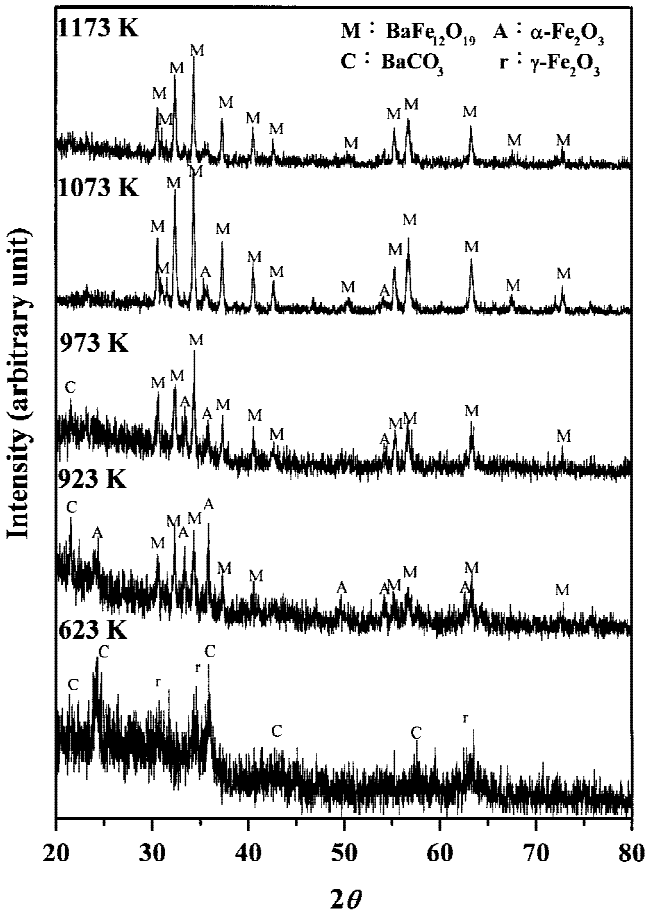

FIG. 4. XRD patterns for the specimens ([citric acid]/[metallic ions] = 1.5 and pH = 9) obtained at different pyrolyzing temperatures.

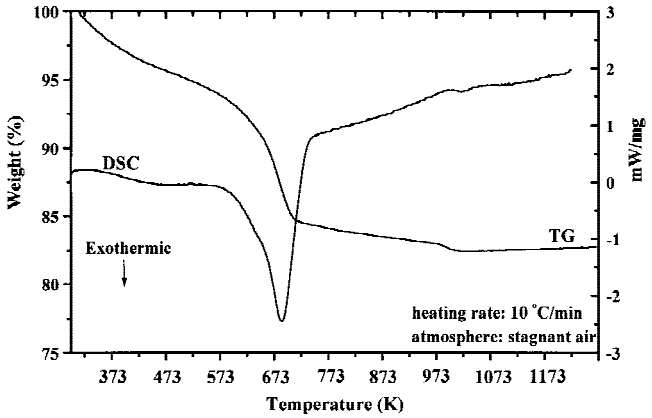

FIG. 5. TG and DSC curves for the specimen ([citric acid]/[metallic ions] = 1.5 and pH = 9) obtained at 623 K.

Step 3

$$6\ \alpha - Fe_2O_3 + BaO \xrightarrow{\Delta} BaFe_{12}O_{19} \quad . \qquad (3)$$

(Fe^{3+} − esters) and (Ba^{2+} − esters) denote that metallic ions in the polyester are mainly ferric ions and barium ions, respectively. (Fe^{3+}, Ba^{2+} − esters) represents that ferric and barium ions, in the stoichiometric ratio to form hexagonal barium ferrite, are uniformly distributed in the ester. The pyrolysis of organic esters would produce gaseous products; depending on elements in the ester and heating temperatures, CO, CO_2, H_2O, and/or NO_x may be evolved. According to the distribution and contents of metallic elements in esters, the prepared solid precursor first decomposes to form $BaFe_{12}O_{19}$, γ–Fe_2O_3, BaO, or $BaCO_3$. The decomposition of esters starts at about 523 K and the resulting $BaFe_{12}O_{19}$ should be in noncrystalline. Noncrystalline $BaFe_{12}O_{19}$ will crystallize when the temperature increases. While γ–Fe_2O_3 transforms to α–Fe_2O_3 during further heating, some γ–Fe_2O_3 reacts with adjacent BaO to form barium ferrite. At temperatures around 973 K, $BaCO_3$ begins to decompose or to react with α–Fe_2O_3. At 1073 K or above, α–Fe_2O_3 reacts with BaO to form $BaFe_{12}O_{19}$.

IV. CONCLUSIONS

This study showed that pure submicron $BaFe_{12}O_{19}$ particles with crystallite sizes less than 200 nm could be produced by pyrolyzing the corresponding ester precursor at 1073 K or above. The molar ratios of citric acid to metallic ions and the pH of starting solutions used in preparation strongly affect the uniformity of metallic ions distributed in the prepared ester precursor. Increasing the molar ratio of citric acid to metallic ions and the pH of starting solutions increases the degree of chelation of the metallic ions in the solutions, which leads to metallic ions more uniform distribution in the ester. The distribution and contents of metallic ions in the ester precursor are key factors in the formation of high-purity barium ferrite powder.

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